

# Fully Resonant Sum and Difference Frequency Mixing Spectroscopy

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High resolution spectra obtained via sum and difference frequency generation are presented for the mixed crystal system azulene in naphthalene. The fully resonant susceptibility  $\chi^{(2)}$  has line narrowing capabilities and predicts dephasing induced resonances related to the PIER-4 and DICE resonances known from  $\chi^{(3)}$  spectroscopy.

## Introduction

The interaction of two light waves with field amplitudes  $E_1$ ,  $E_2$  and frequencies  $\omega_1$ ,  $\omega_2$  leads to the generation of new light waves at the sum and difference frequencies  $\omega_1 + \omega_2$  and  $\omega_2 - \omega_1$ . The source for these new waves are the nonlinear polarizations:

$$\begin{aligned} P_{\text{SUM}} &= \chi_{\text{SUM}}^{(2)} \cdot E_1 E_2 \\ P_{\text{DIF}} &= \chi_{\text{DIF}}^{(2)} \cdot E_1^* E_2 \end{aligned}$$

The susceptibilities  $\chi^{(2)}$  contain information about the level structure and dynamics of the sample molecules. When the fre-

quencies are chosen close to resonance with a three level system  $a < b < c$  the dominant contributions to  $\chi^{(2)}$  are [1]:

$$\chi_{\text{SUM}} = \frac{\mu_{ab} \mu_{bc} \mu_{ca}}{(\omega_{ba} - \omega_1 + i\Gamma_{ab})(\omega_{ca} - \omega_1 - \omega_2 + i\Gamma_{ac})}$$

$$\chi_{\text{DIF}} = \frac{\mu_{ca} \mu_{ab} \mu_{bc}}{(\omega_{ba} - \omega_1 + i\Gamma_{ab})(\omega_{ca} - \omega_2 - i\Gamma_{ac})}$$

$$\cdot \left\{ 1 + i \frac{\Gamma_{bc} - \Gamma_{ac} - \Gamma_{ab}}{[\omega_{cb} - (\omega_2 - \omega_1) - i\Gamma_{bc}]} \right\}$$

(2)

where  $\mu_{ij}$  are the transition dipole moments,  $\Gamma_{ij}$  the phase relaxation rates, and  $\omega_{ij} = (E_i - E_j)/\hbar$  the transition frequencies for each level pair  $ij$ . The difference frequency process contains two time ordered diagrams with different ordering [1]. The interference between these two terms results in a so-called DICE resonance (Dephasing Induced Coherent Emission) which is absent when the pure dephasing parameter  $\Gamma = \Gamma_{bc} - \Gamma_{ab} - \Gamma_{ac}$  vanishes. Such resonances are known from certain  $\chi^{(3)}$  processes where they appear pressure induced in gas phase [2, 3] and temperature induced in condensed phase [4, 5]. The sign of the relaxation parameters  $\Gamma_{ab}$  and  $\Gamma_{ac}$  in the resonance denominators are different for  $\chi_{\text{SUM}}$  and  $\chi_{\text{DIF}}$ , resulting in different line narrowing capabilities for both processes when averaged over inhomogeneous distributions [1].

$\chi^{(2)}$  has been neglected so far for spectroscopic applications since this susceptibility vanishes in centrosymmetric media in the dipole approximation. Polar guest molecules doped into centrosymmetric host crystals form polar guest lattices with pairwise degenerate level systems whose contributions to  $\chi^{(2)}$  cancel each other. Application of a DC electric field will lift the degeneracy (pseudo Stark splitting) [6]. The choice of resonant frequencies  $\omega_1$  and  $\omega_2$  will allow spectroscopy with one sublattice only as shown schematically in Fig. 1. This Stark field induced variant extends the applicability of the method to a large number of mixed crystal systems. In addition the non-resonant signal generated by the centrosymmetric host material will be very small, making the method essentially background free.

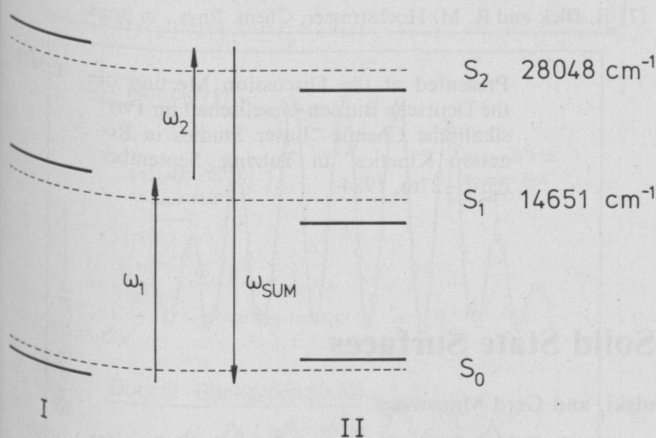


Fig. 1

Schematic representation of sum frequency mixing in the three level system of the azulene vibrationless levels  $S_0$ ,  $S_1$ , and  $S_2$  in the azulene/naphthalene mixed crystal. The Stark shifts are indicated for both sublattices with respect to the zero field case (broken lines), with the ingoing frequencies chosen in resonance with the sublattice I

## Results and Discussion

The spectral lineshapes  $|\chi^{(2)}|^2$  for the Stark field induced spectra are found from Eq. (2) through incorporation of the Stark shift into each  $\omega_{ij}$  and summation over all sublattices.

The simulations in Fig. 2 are based on the parameters for the mixed crystal system azulene in naphthalene having one substitutional site and two sublattices. The intensity of the generated wave is given as a function of the detuning of both laser frequencies from resonance. The top part shows the situation expected for Stark field strengths leading to level shifts still smaller than the level widths. In the middle part the Stark field was assumed to completely separate the sublattices. The two lower plots show the behaviour of  $\chi^{(2)}$  when averaged over an inhomogeneous distribution.

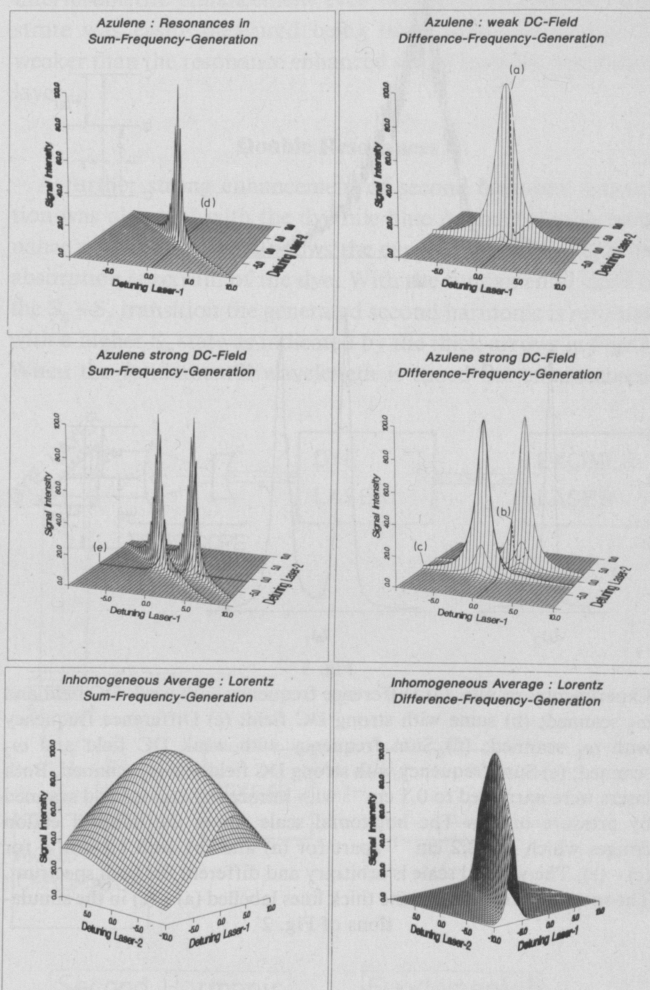


Fig. 2

Simulation of Stark field induced sum frequency spectra (left column) and difference frequency spectra (right column) in the system azulene/naphthalene. Top: weak DC field. The splitting of levels is smaller than the level widths. Middle: strong DC field. Bottom: Convolution of the spectra in the top row with a broad inhomogeneous distribution modelled by a Lorentzian with FWHM of  $20.0 \text{ cm}^{-1}$ . The parameters used are:  $\Gamma_{01} = 1.00 \text{ cm}^{-1}$ ,  $\Gamma_{02} = 0.25 \text{ cm}^{-1}$ , and  $\Gamma_{12} = 1.25 \text{ cm}^{-1}$  corresponding to the low temperature limit of vanishing pure dephasing. The ratio of the Stark splitting of levels  $S_1$  and  $S_2$  is 1.1. The vertical scale is normalized to the maximum value in each case

The spectra are dominated by the linewidth parameters  $\Gamma_{ab}$  and  $\Gamma_{ac}$  corresponding to the  $S_0$ - $S_1$  and  $S_0$ - $S_2$  transitions in azulene. In the difference frequency spectra these resonances appear directly in scans of  $\omega_1$  and  $\omega_2$ . Fig. 3 shows the experimental results. The spectra correspond to the thick lines in the simulation labelled with the same letter. In sum frequency

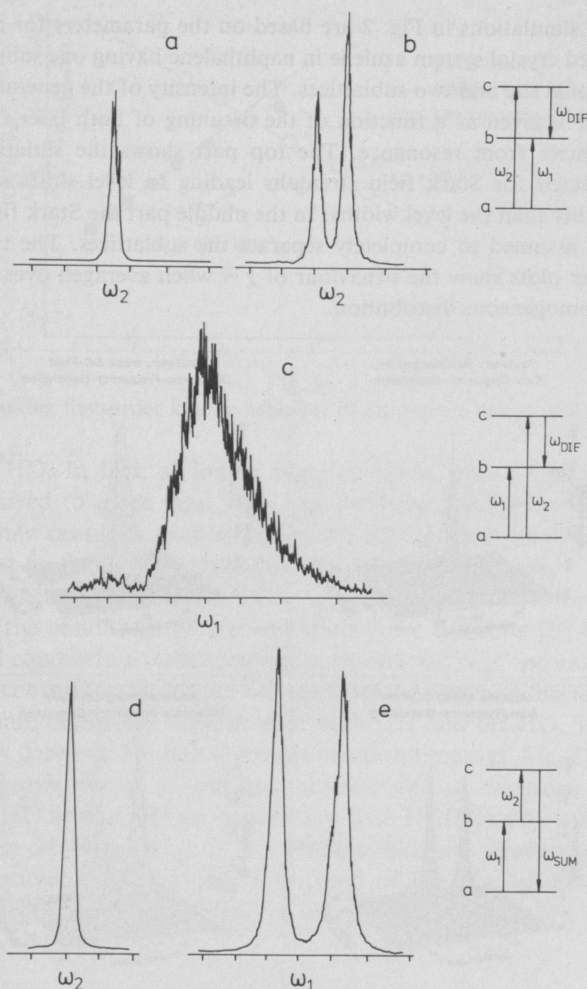


Fig. 3

Experimental results. (a) Difference frequency with weak DC field and  $\omega_2$  scanned; (b) same with strong DC field; (c) Difference frequency with  $\omega_1$  scanned; (d) Sum frequency with weak DC field and  $\omega_2$  scanned; (e) Sum frequency with strong DC field and  $\omega_1$  scanned. Both lasers were narrowed to  $0.1 \text{ cm}^{-1}$  with intracavity etalons and scanned by pressure tuning. The horizontal scale shows the monitor etalon fringes which are  $2.2 \text{ cm}^{-1}$  apart for (a) and (b), and  $1.1 \text{ cm}^{-1}$  for (c)–(e). The vertical scale is arbitrary and different for each spectrum. The spectra correspond to the thick lines labelled (a)–(e) in the simulations of Fig. 2

generation scans of  $\omega_1$  and  $\omega_2$  both yield the narrower width  $\Gamma_{ac}$ , whereas the  $\Gamma_{ab}$  resonance lies along the line  $\omega_1 + \omega_2 = \text{const}$ . Representative scans of  $\omega_2$  (weak DC field) and  $\omega_1$  (strong DC field) are shown in Figs. 3d and 3e. In sum frequency the  $\Gamma_{ab}$  resonance was found by mapping out the  $\omega_1$   $\omega_2$  plane with repeated scans of  $\omega_2$  for various settings of  $\omega_1$  and vice versa. A detailed description of the experiments and results will be given elsewhere [7].

The method has promising aspects for line narrowing spectroscopy as exemplified in the lower part of Fig. 2. A broad inhomogeneous distribution has been superimposed on both the  $S_0$ - $S_1$  and  $S_0$ - $S_2$  transitions with the additional assumption of full correlation between both distributions [1]. The sum frequency spectra reflect just the broad inhomogeneous widths, whereas the difference frequency spectra show a mixture of the homogeneous linewidths. The picture is reversed for assumed anticorrelation of the inhomogeneous distributions. Strict correlation is realized in the Doppler distribution, whereas the degree and sign of correlation is usually unknown for solids.

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## Nonlinear Optics at Solid State Surfaces

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*Methods and Systems / Non-linear Phenomena / Spectroscopy, Ultraviolet / Spectroscopy, Visible / Surfaces*

We have studied the process of optical second harmonic generation in thin surface layers between centrosymmetric materials. The surface susceptibilities are dominated by the electronic properties of adsorbed monolayers of dye molecules. Through the appropriate choice of dye one or two electronic resonances can be employed in the process leading to dramatic enhancement of the generated signal.

### Introduction

When a strong laser beam hits the boundary between two dielectric media, two waves at the second harmonic frequency are generated in forward and backward direction [1]. In piezoelectric crystals these waves are determined by the second order

susceptibility  $\chi^{(2)}$  of the bulk, and the reflected wave can be used to measure this tensor [2]. When both media are centrosymmetric, however, the bulk contributes only quadrupole terms, and all dipole contributions are confined to the thin surface layer where inversion symmetry is broken. The reflected